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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

INFORMATION CIRCULAR

ZIRCONIUM

PART I. GENERAL INFORMATION

BY

E. P. YOUNGMAN

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Z I R C O N I U M[1]

PART I. GENERAL INFORMATION

By E. P. Youngman[2]

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1 - The Bureau of Mines will welcome the reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from the U. S. Bureau of Mines Information Circular 6455."

2 - Rare metals and nonmetals division.

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INTRODUCTION

Before the World War the use of zirconium and its compounds was largely experimental and confined almost wholly to Germany and Austria. Occasionally small lots of zirconium ore had been produced in the United States (1,000 pounds in 1869, 26 tons in 1883, and 3,000 pounds in 1903) and used (with monazite) in the manufacture of various lighting devices, especially incandescent gas mantles; but it was not until 1906 that the discovery of the natural zirconium oxide in large quantities near Sao Paulo, Brazil, first gave promise that a zirconium industry eventually might be developed. Edward Rietz, who worked the Brazilian deposits, interested German chemists in extending the use of zirconium, and by 1911 trade journals were listing German firms as manufacturers of compounds or products derived therefrom. For a time zirconia was one of the various oxides used in the Nernst lamp. It was used also for crucibles and hearths as refractory material; in the manufacture of chemical utensils; in enamels; in the place of bismuth subnitrate for defining Röntgen-ray pictures of the stomach; as a pigment; in medicine; and in a number of other ways. The Germans were credited also with producing a remarkable zirconium steel, which, it was claimed, was much superior to other alloy steels.

During the World War the United States Government investigated the possibilities of zirconium, as well as those of other steel-hardening elements, and a large automobile manufacturer actually purchased a substantial quantity of ore with the purpose of employing zirconium in automobile steels. Immediately after the armistice the Government ceased its investigations; but despite the difficulties experienced by various investigators in reaching concordant results, interest in the use of zirconium as a steel-hardening agent, as well as in other uses of the element and its compounds, continued. In 1918 the Foote Mineral Co., which had been interested in zirconium for several years, was exploiting the deposit in Brazil formerly worked by the Germans and was supplying zirconia in the form of ore, brick, and cement for refractory and other purposes. About the same time the Electro Metallurgical Co., which before the entrance of the United States into the war was experimenting with zirconium alloys, supplied in tonnage quantities the demand for these alloys. In 1919 it was reported that American manufacturers, after several years of research, were producing in commercial quantities pure zirconium oxide, which was finding a place in the manufacture of small refractory articles, scorifying dishes, crucibles, tubes, and one-piece furnace linings.

In 1920 the lowering of the price of zirconium metal powder (because of improved metallurgical methods) promised the production of the metal on a semicommercial scale. In 1924 the Titanium Alloy Manufacturing Co. introduced a new opacifying agent, "Opax," made from zircon. A year or two later some of the large pottery manufacturers became interested in the use of zirconium oxide as an opacifying agent, the increased production of titanium pigments having resulted in the production of zirconium as a by-product at a price that could compete with tin oxide. In 1928 it was reported that the industrial use of zirconium oxide was increasing steadily in the manufacture of brick, crucibles, and other refractory products, such as high-temperature cements. However, the reluctance of producers to install additional and more suitable

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machinery for sorting and concentrating the ore was limiting somewhat the manufacture of these products. In 1929 the report was that, although a shortage of high-grade ore existed, the use of zirconium in enamels for opacifying and its use as a refractory material had increased. In 1930 the Foote Mineral Co. reported greatly increased use of zirconium oxide as a refractory.

DESCRIPTION AND PROPERTIES

Zirconium falls into Group IV of the periodic system. Its position in this group, previously indicated by its analogies with the elements of the fourth group, was first confirmed by means of the high-frequency spectrum. As might be expected from their relative positions in the periodic table, zirconium resembles titanium in many of its characteristics and has properties in common with germanium also.

As zirconium is an exceedingly difficult metal to isolate, conflicting statements have been made with respect to its nature and properties; and, according to Lee,[3] most of the data with respect to zirconium, painfully acquired during a century and a half, must now be revised as a result of the discovery that the substance formerly considered an element is really a mixture of two elements, one zirconium and the other hafnium.

Description of the Metal

In a reasonably pure condition (as far as it has been prepared), 99.69 to 99.89 per cent, the metal is known as an amorphous black powder, which is steel-gray in color when melted, and which gives a lustrous metallic mirror when burnished. The existence of crystalline and graphitic forms has been claimed but not proved, according to Venable,[4] who states that investigators reporting them had alloys rather than the pure metal at hand. Marden and Rich seem to agree with this conclusion of Venable. In discussing the different forms of the metal, they refer to the "so-called" crystalline zirconium prepared by Troost and refer also to the method for the preparation of the graphitic zirconium (first used by Troost) as a doubtful one for the production of a pure metal.[5] According to these same authors,[6] the coherent (or sintered) metal shows decided crystalline structure under the microscope, but many of the references in the literature to crystalline zirconium describe the aluminum alloy.

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3 - Lee, O. Ivan, The Mineralogy of Hafnium: Chem. Reviews, vol. 5, No. 19, Am. Chem. Soc., 1928, p. 35.
4 - Venable, Francis P., Zirconium and its Compounds: Am. Chem. Soc. Monograph Ser., The Chemical Catalog Co. (Inc.), New York, N. Y., 1922, p. 26.
5 - Marden, J. W., and Rich, M. N., Investigations of Zirconium with Especial Reference to the Metal and the Oxide: Bull. 186, Bureau of Mines, 1921, pp. 36-37.
6 - Marden, J. W., and Rich, M. N., Work cited, p. 37.

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Properties of the Metal

The melting point of zirconium is 2,130°C. The specific gravity of hafnium-free zirconium is 6.52, and its atomic volume is 13.97.[7] The atomic weight of the metal is 90.6; its hardness, 6.7; its specific refraction, 0.242; and its atomic refraction, 21.9.[8]

Pure zirconium rods produced by thermal decomposition of zirconium tetraiodide can be worked, although rods made from zirconium powder can not be. The workable rods may be hammered, rolled out, and drawn to thin filaments, having a diameter of less than .0008 inch.

Chemically, zirconium is a very reactive metal. It is readily attacked by hydrofluoric acid, hot concentrated sulphuric acid, and aqua regia. Concentrated hydrochloric acid, however, acts upon it only slightly and nitric acid not at all. It combines with all gases, except the rare gases. Amorphous zirconium when heated below 700° absorbs hydrogen, forming a solid hydride, which is fully dissociated at 800°. Zirconium combines readily with oxygen, burning with a bright light when heated even much below red heat; the denser and purer metal oxidizes only slowly when heated in air up to 270°. Amorphous zirconium readily combines with nitrogen; and when heated with carbon it forms a carbide, which if rich in carbon is gradually decomposed in air but which otherwise remains stable. At high temperatures, the metal readily combines with silicon and boron. Zirconium when heated and acted upon by chlorine and bromine forms tetrahalides; when heated and passed over by ammonia it forms the nitride. Sulphur combines with heated zirconium. Red phosphorous combining with zirconium gives a black powder. Zirconium forms alloys with copper, silver, aluminum, metals of the iron group, and others, but not with tin or lead.[9]

In a comparatively recent contribution to the trade literature, De Boer[10] says of zirconium metal, especially of that produced by his own processes, that it has a specific electrical resistance, at 0°C., of 41 times 10^{-6} ohms per cm^3; a temperature coefficient of resistance, at 0 to 100°C., of 0.0044; a coefficient of linear thermal expansion, at room temperature, of 6.3 times 10^{-6}; and an electron emission of 1.3 milliamperes per square centimeter at 1,700° K. Zirconium has about the same electron emission at 1,700° K. as thorium at 1,400° K. and tungsten at 2,000° K. (See also article by De Boer referred to in footnote 7.)

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7 - De Boer, J. H., Zirconium: Foote-Prints on the Rare Metals and Unusual Ores, vol. 3, No. 2, Foote Mineral Co. (Inc.), Philadelphia, Pa., 1930, p. 18.
8 - Venable, Francis P., Work cited, pp. 27-28.
9 - Venable, Francis P., Work cited, p. 30.
10- De Boer, J. H., Zirconium: Ind. Eng. Chem., vol. 19, No. 11, Am. Chem. Soc., Nov., 1927, pp. 1256-1259.

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Description of the Oxide

The only definitely known oxide of zirconium is the dioxide, which occurs in nature as baddeleyite, and which can be made in the laboratory by the ignition of different zirconium compounds, as the sulphate, the oxychloride, and the hydroxide. According to Marden and Rich,[11] zirconia (ZrO_2) exists in two forms, amorphous and crystalline. The amorphous zirconia is a white powder of flourlike appearance when finely pulverized and is exceedingly inert toward chemical agents. This is the form that is generally produced in the laboratory or in industrial plants. Crystalline zirconia, according to De Boer,[12] has at least three crystal modifications (monoclinic, pseudoregular-tetragonal, and pseudohexagonal-rhombic forms).

Properties of the Oxide

As is the case with the metal, statements with respect to the properties of the oxide vary with different authors. In a very recent article, De Boer[13] gives the following data:

> The density of the monoclinic form is 5.56; that of the tetragonal form is 6.10.
>
> The melting point is very high, 2,950° ± 20° K. The oxide is a good insulator for heat and electricity. The coefficient of expansion is about 8.10^{-7}, only a little higher than that of silica, at least when the oxide has been melted before. Corresponding to the change in modification, there is a contraction at about 1000° C. Heated in an oxyhydrogen flame, the oxide gives a brilliant white light.
>
> The hardness of well-ignited zirconium dioxide (a hard, white powder) lies between 6 and 7.
>
> From a chemical point of view, zirconium dioxide is a very stable product. This can be seen from the exceptionally high heat of formation, which is 264.0 K. cal. per mol. (out of metal and oxygen). When it is ignited, it is practically insoluble in all acids, except hydrofluoric acid, which dissolves it with a very violent reaction, provided the oxide was not ignited at too high a temperature. It is attacked by melted alkali bisulphate, caustic alkalies, or alkali carbonates. Heated with carbon, it will yield the carbide ZrC. Heated with carbon in a chlorine stream, it gives the tetrachloride.

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11 - Marden, J. W., and Rich, M. N., Work cited, p. 20.
12 - De Boer, J. H., Zirconium: Foote-Prints on the Rare Metals and Unusual Ores, vol. 3, No. 2, Foote Mineral Co. (Inc.), Philadelphia, Pa., 1930, pp. 6-7.
13 - De Boer, J. W., Work cited, pp. 7-8.

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For a description of the nature and properties of the other compounds of zirconium, the reader is referred to the works of Venable,[14] of Marden and Rich,[15] and of De Boer,[16] quoted in preceding paragraphs.

HISTORY OF THE ELEMENT

The following chronology gives the names of scientists connected with the discovery of the element and its history step by step.

1789--Klaproth, while studying samples of the mineral zircon from Ceylon, found a large amount of an oxide resembling alumina closely but differing from it in being insoluble in alkalies. To this oxide the name "zirconium" was given, a name that is probably a corruption of "jargon," a Persian word meaning gold-colored.

1818--Berzelius pointed out the resemblance of the oxide to alumina and gave it the formula Zr_2O_3.

1824--Berzelius prepared the metal as an iron-gray powder by reducing potassium fluozirconate with potassium.

1845--Svanberg announced his belief that the oxide is a mixture of at least three earths; and he reported the new earth noria.

1857--Deville and Troost determined the vapor density of the chloride, that the element is quadrivalent, and that the formula ZrO_2 must be assigned to the oxide.

1859--Rose showed that the formula ZrO_2 was in accord with the isomorphism of rutile (TiO_2) and zircon (ZrO_2,SiO_2).

1860--Marginac observed the isomorphism between the fluozirconates of zinc and nickel and the fluosilicates, fluotitinates, and fluostannates of these metals.

1864--Nylander claimed that he had separated the new oxides from zirconia.

1865--Troost claimed that he had prepared the crystalline metal.

1869--Sorby and Forbes announced the discovery of jargonia, a new oxide. Church found the new element nigrium.

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14 - Venable, Francis P., Work cited, pp. 35-125.
15 - Marden, J. W., and Rich, M. N., Work cited, pp. 13-19.
16 - De Boer, J. H., Zirconium: Foote-Prints on the Rare Metals and Unusual Ores, vol. 3, No. 2, Foote Mineral Co. (Inc.), Philadelphia, Pa., 1930, pp. 6-13.

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1901--Hofman and Prandtl claimed to have separated euxenerde from the zirconia of euxenite.

1923--Coster and Hevesy announced that examination of the X-ray spectra of the commoner zirconium minerals disclosed the presence, often in considerable quantity, of element 72 (for which they proposed the name "hafnium"), which remains closely associated with zirconium in the extraction of that element and is not easily separated from it.

USES

The first recorded use of zirconium or its compounds was the employment of the natural silicate as gem material. Zircon jewelry had been sold in very small amounts for many years, and recently zircon stones have become much more popular, largely owing to the introduction of the so-called "blue variety," named "Starlite" by Dr. Kunz.

The widest application of zirconium at the present time, however, is the use of the oxide as refractory material; and the second most extensive use, it is claimed, is that of the oxide as an opacifying agent, especially in enamel ware, as a substitute for tin oxide. Likewise, the use of the oxide as an opacifier in lacquers and automobile enamels seems to be of increasing importance.

Growing utilization of the pure metal is indicated by the decided drop in prices in 1929. Also more extended use of the metal alloys in steel is signified by a definite increase, in 1929, in the imports into the United States of steel-hardening ore.

Refractory Uses

Both zirconia (the pure zirconium oxide) and zirkite (the native Brazilian oxide or a semimanufactured form carrying 75 to 85 per cent of oxide) are employed as refractory material; however, as the pure oxide is too costly for large-scale industrial use, zirkite is generally substituted.

Because of its high fusing point (about 3,000° C.), zirconia is one of the most refractory oxides known. It does not melt below 2,560° C. even when it contains approximately 1.25 per cent of silica and ferric oxide. The pure fused material has very low thermal conductivity and a very low coefficient of expansion (8.4 times 10^{-7}), which compares favorably with that of carborundum (6.58 times 10^{-6}) or alundum (7.1 times 10^{-6}). Zirconia withstands sudden changes of temperature remarkably well, and it is chemically inert, being highly resistant to acids, fused quartz, and molten glass, and to a large extent even to fused alkalies. Under certain conditions, however, it has a tendency to be changed at high temperatures into a nitride or a carbide.[17]

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17 - Rodd, E. H., Zirconia as a Refractory: Mineral Foote-Notes, July-Aug., 1918, Foote Mineral Co., Philadelphia, Pa., 1918, p. 7.

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Brick

Improved methods of working zirconia into bricks and the addition of minimum quantities of magnesia or lime to obviate their former tendency to crack have greatly increased the use of zirconia or zirkite bricks. The various standard shapes are finding wide application in the United States, especially for lining electric furnaces.

With respect to the qualities of this form of refractory material, La Coultre and Carl[18] stated that the softening temperature for zirconia brick is 900° C. higher than that of fire clay and 600° higher than that of carborundum. The melting point of the brick, 2,600° C., is the same as its softening temperature. Zirconia bricks are inert to chemical influence; they are not attacked by hydrofluoric acid or by bisulphates; they are almost twice as brittle as fire clay or silica bricks and six times as brittle as alumina bricks; their compressive strength is nearly double that of fire clay; their tensile strength is much greater than that of other refractories; and their wear in furnaces is much less than that of silica bricks. The greater wearing quality of the bricks insures longer life and reduction in repair charges for a furnace, compensating for the higher initial cost of the bricks.

With respect to manufacturing processes for zirkite bricks, Meyer says[19] that the American method of manufacture consists essentially:

> ------In first passing the ore through a crusher and grinding it to about 60-mesh in a dry pan, removing all particles running finer than 100-mesh by passing it over inclined screens and bonding the resulting product with zirkite cement. About 50 per cent of 60-mesh zirkite and 50 per cent of zirkite cement constitute the refractory mass. This is made into a stiff mud with water and moulded in the same fashion as silica brick. "Green" zirkite bricks have to be dried very slowly, as otherwise they develop air cracks. Furthermore, great care should be exercised in setting them, as they are very brittle in the unburnt state. The percentage of loss is rather high, but the warpage and cracked bats can be used over again after regrinding in the dry pan.

Cement

The Foote Mineral Co. offers "Zirkite" cement in two grades, both of high-melting point, low coefficient of expansion, low thermal conductivity, and high resistance to corrosive slag and gases. One grade, the plastic grade (in the form of dry powder), carries 75 to 80 per cent of pure zirconium oxide,

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18 - La Coultre,_____, and Carl,_____, Zirconia Bricks: Chem. Age, vol., 17, London, Oct. 1, 1927, pp. 28-29 (of the Monthly Metall. sec.).

19 - Meyer, H. C., Zirconia; Its Occurrence and Application: Trans. Ceramic Soc., vol. 18, 1918-19, Stoke-on-Trent, 1919, p. 273.

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has a softening point of 1,750 to 1,800°C., and sets at room temperature to a hard mass within a few hours. It is especially suitable for rammed-in linings or patchings. The nonplastic grade, which lends itself especially to "laying up zirkite bricks," does not harden at room temperature but at a temperature of about 500° C.

Another product, trade-marked "Zirkonalba," a chemically pure oxide, is used as a cement and also in the manufacture of articles subjected to exceptionally high and rapid fluctuations of temperature or to the corrosive action of slags and furnace gases. A melting point of 2,500 to 3,000° C. (4,503 to 5,432° F.) is claimed for Zirkonalba.[20]

Laboratory Ware

With respect to the manufacture of highly refractory utensils for laboratory equipment and similar ware, Meyer states[21] that zirkite filtering crucibles, muffles, combustion tubes, combustion boats, pyrometer tubes, and Kipp generators, with replaceable units, are now on the market at prices that compare favorably with like articles of porcelain or fused silica; that combustion tubes have run in steel-testing laboratories on carbon determinations for as long a period as three months, in constant use day and night; that because of the composition of these tubes they are not attacked by basic substances, do not devitrify, and are gas-tight up to temperatures of 1,000° C.

According to the Bureau of Standards,[21] zirconia crucibles (cast and fired as described below) have proved to be satisfactory for melting platinum (melting point, 1,755° C.) and rhodium (melting point, 1,950° C.) in air in high-frequency furnaces. These crucibles, which are best when made with an outer supporting crucible of alundum or porcelain, with the annular space packed with dry, purified zirconia, as they do not withstand sudden temperatures as well as could be desired, have been successfully used for making laboratory melts of platinum and platinum-rhodium alloys up to 300 or 350 grams in weight. The process of manufacture of this type of crucible is as follows:

> Commercial, electrically sintered and milled zirconia is washed three or four times, or until the washings are free from iron, in hot 1 : 1 hydrochloric acid. The acid-washed and dried zirconia is then roasted in an electric muffle furnace at 800 to 900° in porcelain evaporating dishes, with free access of air and with frequent stirring in order to burn out the carbon or carbides.
>
> The purified zirconia is then prepared as a casting "slip" by grinding with water and a small amount of china clay in a porcelain

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20 - Mineral Foote-Notes, Zirconia: Vol. 3, No. 1, Foote Mineral Co., Philadelphia, Pa., 1930, p. 62.

21 - Meyer, H. C., Work cited, pp. 274-275.

22 - Jordan, Louis, Peterson, A. A., and Phelps, L. H., Refractories for Melting Pure Metals; Iron, Nickel, Platinum: Trans. Am. Electrochem. Soc., vol. 50, 1927, pp. 162-164.

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ball mill with flint pebbles. The ball-mill charge is made in the proportions of 1,000 grams of purified zirconia, 40 grams of china clay, and 500 cubic centimeters of water. After grinding for approximately 8 hours, this slip is in a suitable condition for casting in plaster of Paris molds.

The cast zirconia crucibles are dried, first in air and then in an oven at 120 to 150° C., and are then fired to 1,700 to 1,800° C. in an Arsem furnace inside a covered protecting crucible of zirconium silicate.

Opacifying Uses

As an opacifier in enamels, as well as a clouding agent in glass, zirconia is an excellent substitute for stannic oxide, antimony oxide, and others. As a result of investigations in Germany, a number of proprietary compounds of zirconium oxide mixed with certain fluxes have been placed on the market, and many foreign patents have been issued covering the use of the oxide in white enamels for steel and cast-iron utensils.

The pure zirconium oxide is, it is claimed, superior to stannic oxide in that it is less easily reduced, is less volatile, and produces an enamel that is more resistant to vegetable and fruit acids. One authority maintains that zirconium compounds are more dependable than other substitutes for stannic acid in the opaquing of white glazes, 5 per cent of the oxide producing a good white glaze, whereas other authorities state that zirconium oxide has less covering power than stannic oxide, and that it is very difficult to obtain an iron-free product.

Minor Uses of the Oxide

The incandescence of zirconium oxide when heated was early taken advantage of in mantles, glowers, and lights. It first replaced the calcium oxide cylinders in the Drummond light; zirconia rods, heated to incandescence, were tried out for lighting Paris streets; an incandescent mantle was made that was composed chiefly of zirconia, which was soon replaced by thoria, however; in the Nernst light, small rods or glowers of zirconium, magnesium, and yttrium oxides were heated by an auxiliary device to a temperature of about 700° C., at which point they became conductors of electricity and through their resistance to the passage of current became incandescent. Except in the Bleriot light, which has been adopted somewhat extensively abroad, the quantity of zirconia employed in these connections is small.

Zirconia, as "Kontrastin," has been substituted for bismuthyl nitrate as a lining for the stomach in connection with X-ray photographs. Because of its hardness, its stability toward chemical reagents, and its volume, zirconia has been suggested for polishing and toilet powders. Small additions of zirconia to fused silica ware prevent devitrification. Finely divided oxide incorporated with rubber before its vulcanization increases its toughness and accelerates the vulcanizing process. Zirconium oxide produces a nonpoisonous, nondiscoloring white paint; it is used in ink, water-color paints, and like products.

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Uses of Other Compounds

The carbide has been patented as a filament for incandescent lamps. It has been suggested as an abrasive, an experimental cement wheel giving good results with mother-of-pearl. It can not be used, however, in ceramic wheels, as it reacts with silicates at high temperatures.

The nitrate has been employed as a food preservative and in the lighting fluids used in the manufacture of incandescent mantles.

The acetate has been used in the place of stannic salts for the weighting of silk, a 50 per cent weighting being feasible.

Zirconium hydroxide has been considered for use in the purification of water. Zirconium compounds are used as mordants in the dyeing industry and in the preparation of lac dyes. Zirconyl tannate may find use as a substitute for sodium tungstate or stannate in rendering cloth noninflammable. The tetrachloride has been suggested as a chlorinating agent.

Uses of the Metal

Probably the chief commercial use of the metal to-day is in flashlight powders. Usually a mixture containing 60 per cent of zirconium and 40 per cent of magnesium is used, with barium nitrate as a primer. Another flashlight device consists essentially of aluminum leaf covered with zirconium-metal paste, which is set off when connected with an electric lighting circuit.

Zirconium metal is employed in radio tubes, in which it acts as a "getter."

Investigators have succeeded in producing a malleable zirconium as a substitute for platinum in the chemical laboratory. The metal is suitable for use in the manufacture of scientific apparatus and most delicate instruments and is said to be an ideal material in dentistry, because of its malleability, ductility, noncorrosiveness, and imperviousness to the action of gases.

The metal is of peculiar value for use on spark plugs, thermocouples in pyrometers, and other instruments for measuring heat, because of its high fusing temperature.

Research work has been carried on with reference to the employment of zirconium for the lining of cylinders of internal-combustion engines and for the manufacture of pistons.

The fact that zirconium has a pronounced electronic valve action is noteworthy, although zirconium electrodes may not, when available, be of great value in connection with valve cells. A new resistor, which has simplified the manipulation of currents used for impulse tests or measuring, has been developed from a so-called "zircon mixture." These zircon rods are particularly suitable for field investigations of lightning disturbances on transmission lines.[23]

23 - Beck, Edward, A New Resistor for Use in Measurements of Impulse Voltages and Currents: Electrical Jour., vol. 25, No. 3, Mar., 1928, pp. 157-158.

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ZIRCONIUM ALLOYS

A few hundred tons of zirconium ore is used annually in the production of zirconium alloys. These alloys, which are produced in electric furnaces, are employed principally in the production of steel castings. The substitution of zirconium-ferrosilicon for the ordinary ferrosilicon makes possible a sounder and cleaner product, which is desirable in steels for castings, forged products, and rolled shapes that must be subjected to repeated and violent shocks. Silicon-zirconium is preferred for removing objectionable gases and nonmetallic impurities in the finer alloy steels.

Although it seems to be generally agreed that zirconium gives to alloyed metals increased tensile strength, toughness, and some degree of malleability, accurate information concerning the properties of zirconium alloys is rather meager, and conflicting opinions are expressed in published statements in the literature. Until very recently the claim was made that zirconium did not alloy with iron, but now ferro-zirconium, zirconium-ferrosilicon, and silicon-zirconium are on the market and are strongly recommended for use in steel, as well as in nickel alloys. Zirconium does not alloy with tin, lead, or metals of the alkali or alkaline-earth groups. Cobalt, aluminum, and magnesium alloys have been placed on the market, and silver alloys have been prepared.

The following summary of the value of zirconium in steel is from the catalog of the manufacturer of zirconium alloys:[24]

> When added to steel, zirconium performs three important functions. By its powerful deoxidizing action it vigorously reduces metallic oxides and scavenges nonmetallic inclusions, but it does not tend to remain in the steel in the form of an oxide, as does aluminum. By reason of the cleansing it thus receives, the steel becomes homogeneous both as to composition and structure. Secondly, zirconium combines chemically with nitrogen dissolved in the steel, forming a nitride of which by far the greater part enters the slag; the few nitride crystals remaining in the steel are too minute to have any effect on its mechanical properties. Finally, zirconium combines chemically with sulphur abstracted from the iron, the resulting sulphide being malleable like that of manganese; moreover the hot-shortness of high-sulphur steel can be diminished through the agency of zirconium to a degree not attainable by manganese, but for economic reasons it is not suggested that zirconium should displace manganese entirely in the treatment of high-sulphur steels.
>
> A zirconium-treated carbon steel is therefore characterized by: freedom from inclusions, which would act as nuclei for shock and fatigue failures; uniformity of grain, which assists in the effectiveness of heat treatment; excellent hot-working properties; and, when suitably heat-treated, tensile properties closely approaching those of special alloy steels, ductility being especially favored by zirconium treatment.

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24 - Electro-Metallurgical Sales Corporation, Carbide and Carbon Bldg., 30 East 42d Street, New York, N. Y.

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The alloy generally used is zirconium-ferrosilicon, which contains 13 or 14 per cent of zirconium and 45 per cent of silicon, and which costs (Jan., 1931) $103.50 a gross ton in carload quantities. Where a large excess of silicon would be undesirable, silicon-zirconium, containing 35 to 40 per cent of zirconium, is used. Its cost, however, is (Jan., 1931) 18 cents a pound.

"Cooperite" is the name given to a patented zirconium-nickel alloy for use in the manufacture of edge tools of all kinds, especially machine tools for milling cutters and cast tools for lathe and plane. When the alloy contains 2 to 10 per cent of zirconium, the remainder being nickel, it is suitable for knives, razors, and like articles, which remain bright and clean under the action of acids such as that of the lemon. Since it can be worked at a red heat, it is applicable for electrical toasters, irons, and other domestic utensils. When the alloy contains 25 to 30 per cent of zirconium, it is suitable for high-speed cutting tools, though some other metal, such as molybdenum, is sometimes added to increase the melting point or the hardness of the metal.

A zirconium-nickel alloy patented by Cooper (composition: Al, 8.36; Si, 3.80; Zr, 6.84; and Ni, 81) was produced as follows:

> Sixty-six pounds of nickel oxide and 36 pounds of Brazilian zirkite were ground to pass a 200-mesh sieve and were thoroughly mixed with 32 pounds of 200-mesh magnesia or alumina. The charge was ignited with magnesium ribbon. The alloys were tapped into molds, remelted, and further purified to give the desired percentage composition.

ZIRCONIUM-BEARING MINERALS

The better-known zirconium-bearing minerals are tabulated by Watson and Hess as follows:[25]

25 - Watson, Thomas, and Hess, Frank L., Properties, Occurrence and Uses of Zircon: Min. Eng. World, vol. 37, July 6 to Dec. 28, 1912, p. 951.

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Mineral	Composition	Inclosing Rock	ZrO_2 Per cent
Oxide:			
Baddeleyite (Brazilite)	ZrO_2	Igneous rocks deficient in silica, and in gravels derived from them	100
Zirconates:			
Zirkelite	$(Ca,Fe)O.2(Zr,Ti,Th)O_2$	Magnetite-pyroxenite (jacupirangite)	52.89
Polymignite	$5RTiO_3.5ZrO_3.R(Cb,Ta)_2O_6$	Elaeolite syenite	29.71
Silicates:			
Zircon	$ZrSiO_4$	Variable, described below	67.2
Cyrtolite	Some cyrtolite is probably hydrated zircon	Granite, pegmatite	66.93
Catapleiite	$H_2(Na_2,Ca)(Zr(OH)_2)(SiO_3)_3$	Elaeolite syenite	28.8
Elpidite	$H_6Na_2ZrSi_6O_{18}$	Elaeolite syenite (?)	20.48
Eudialyte (Eucolite)	$Na_{13}(Ca,Fe)_6.Cl(Si,Zr)_{20}O_{52}$	Elaeolite syenite	16.88
Hainite	Related to lavenite, wohlerite, etc.	Phonolite	Unknown
Hjörtdahlite	$4Ca(Si,Zr)O_3.Na_2ZrO_2F_2$	Elaeolite syenite	21.48
Lavenite	$(Na_4,Ca_2,Mn_2,Zr)((Si,Zr)O_3)_2$	Elaeolite- or augite syenite	31.65
Lorenzenite	$Na_2Si_2(Ti,Zr)_2O_9$	Pegmatite	11.92
Rosenbuschite (Zircon pectolith)	$Na_2Ca_3((Si,Zr,Ti)O_3)_4$	Elaeolite syenite	20.10
Wöhlerite	$(Na_2,Ca)(Si,Zr)O_3.RCb_2O_6$	Zircon syenite	22.72

The orthosilicate zircon and the oxide baddeleyite are practically the only zirconium minerals of commercial importance, but certain of the others, notably eudialyte and the altered zircons, alvite, cyrtolite, and malacon, have recently become of scientific interest, in that they have been proved to be among the richer hafnium-bearing minerals.

Zircon

Zircon, the most widely distributed and the most abundant zirconium mineral, is an orthosilicate, having the formula $ZrSiO_4$, and containing (when pure) 67.2 per cent of zirconia and 32.8 per cent of silica. Frequently iron is present in small quantities. Zircon occurs in crystals and in formless grains. The crystals are tetragonal, commonly in square prisms, sometimes elongated, having pyramidal terminations. The crystals sometimes show geniculated twinning. Large perfect crystals are rare and, when found, are classed as gems.

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Zircon is harder than quartz (hardness, 7.5) and fairly heavy (sp. gr. 4.7). The molecular weight is 183, and the molecular volume is 38.7. It is infusible, and it is insoluble in most acids but is attacked when in powdered form by concentrated sulphuric acid. It is brittle, has imperfect cleavage, conchoidal fracture, and adamantine luster. It is generally opaque, and the color is usually some shade of brown, although it may be clear yellow, gray, green, red, or some other color, or (rarely) colorless.

Mode of Occurrence

Zircon occurs (1) as a product of magmatic segregation, (2) in pegmatite dikes, (3) occasionally as a product of contact metamorphism, and (4) as a product of dynamo-regional metamorphism.[26] Classes 1 and 2 constitute the principal sources.

As an accessory constitutent, zircon is found in nearly all classes of plutonic and volcanic rocks. It is a very common constituent of granites and syenites and occurs in some diorites and gabbros (among plutonic igneous rocks) and in quartz-porphyry, trachyte, phonolite, tephrite, dolerite, diabase, and basalt (among volcanic igneous rocks).

Zircon is a frequent associate in beds of sand and gravel, and hence, it is found in various sedimentary rocks, including even limestones. On account of its density, it is one of the minerals left behind by transporting agencies; so that it is a natural concentrate in river and sea sands and gravel. Its high degree of hardness enables it to resist wear as it is being carried by running water, and its great durability enables it to resist weathering.

Zircon, occurring in almost all classes of metamorphic crystalline rocks, is found especially in gneisses rich in feldspar that are of probable igneous origin and also in different types of crystalline schists, particularly the hornblendic, chloritic, and micaceous groups. It is usually found also in quartzites.

Zircon has been noted as an accessory mineral in iron-ore deposits, particularly magnetite deposits.

Identification

According to Zealley,[27]

> *****zircon is easily recognized by its physical properties and by the following simple blowpipe test: Fusing the powdered mineral with sodium carbonate, dissolving the melt in dilute hydrochloric acid, and adding turmeric paper. The presence of zirconia is revealed by the paper's turning to an orange color.

26 - Watson, Thomas L., and Hess, Frank L., work cited, p. 952.
27 - Zealley, A. E. V., Zirconium Ore: Rept. Rhodesian Resources Committee, 1921, Bulawayo, 1921, p. 130.

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Baddeleyite

Baddeleyite, much less widely distributed than zircon, is the dioxide of zirconium (ZrO_2). This mineral has been found in quantity in Brazil only; however, it has been identified in Ceylon, Sweden, Italy, and Montana. In fibrous, botryoidal, or columnar forms, the oxide is termed "brazilite," whereas the name "baddeleyite" refers to the mineral when it occurs in distinct crystals. Jacupirangite is the name applied to a crystalline variety of baddeleyite, named from Jacupirangi (or Jacupiranga), Brazil. Baddeleyite is not quite so hard as zircon (hardness, 6.5) but is heavier (specific gravity 5.5 to 6.0). The crystals are colorless, yellow, brown, or black.

ZIRCONIUM ORES

As previously noted, zircon and baddeleyite are the only zirconium-bearing minerals occurring in sufficient abundance to form ore deposits. The following table is a convenient classification of commercial minerals.

Commercial classification of zirconium ores[1]

Name			Formula	Per cent ZrO_2
Baddeleyite (distinct crystals)			ZrO_2	96.5-98.9
Brazilite			ZrO_2	71.93
Zircon			$ZrO_2.SiO_2$	67
Zirconia ore:	1. Favas (alluvial pebbles)		ZrO_2	59-92.4
	2. "Zirkite" (mixture)	(Brazilite	ZrO_2	71.93
		(Zircon	$ZrO_2.SiO_2$	67
		(Unnamed Zr silicate		
		(Orvillite (?)		

1 Lee, O. Ivan, The Mineralogy of Hafnium: Chem. Rev., vol. 5, No. 19, Am. Chem. Soc., 1928, p. 18.

In the trade, the name "baddeleyite" seems to be confined to the variety in distinct crystals and the name "brazilite" to the fibrous, botryoidal, or columnar form. The trade name "Zirkite" is applied to a mixture of baddeleyite or brazilite, zircon, and a supposed new and unnamed silicate of zirconium. Zirkite contains from 70 to 94 per cent of zirconium oxide. The following variations in the analyses of commercial ores were reported by Schaller:[28]

28 - Schaller, Waldemar T., Zirconium and Rare-Earth Minerals: Mineral Resources of the United States, 1916, pt. 2, U. S. Geol. Survey, 1919, p. 377.

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Analyses of zirkite

	1	2	3	4	5	6	7	8	9	10	11
ZrO_2	93.18	81.75	86.57	85.93	82.00	85.01	71.88	94.12	88.40	74.48	68.93
SiO_2	1.94	15.49	2.50	9.35	11.38	9.63	25.31	2.41	5.89	14.08	26.30
TiO_2	.69	.50	1.43	1.84	.36	1.52	.63	.98	3.12	1.35	.60
Fe_2O_3	2.76	1.06	5.29	1.93	2.08	3.57	.43	3.22	4.07	10.26	3.59
Al_2O_3	.64	.85	1.00	.36	.62	--	.15	--	--	--	--
MnO	Trace	Trace	--	--	--	--	--	--	--	--	--
H_2)	.47	.63	3.32	1.56	3.35	--	1.56	--	--	--	.80
	99.68	100.28	100.11	100.97	99.79	99.73	99.96	100.75	101.48	100.17	100.22

1. Slate-gray fava (waterworn pebble resembling a bean). Specific gravity 5.245.
2. Light-brown fava. Specific gravity 4.850.
3-6. Hard lump ore.
7. Gray porous ore.
8. Glassy variety.
9. Stony variety.
10. Pebbles.
11. Commercial variety.

Analyses of baddeleyite

	1	2	3		1	2	3
ZrO_2	97.19	98.90	96.52	MnO	Trace	--	--
SiO_2	.48	.19	.70	MgO	--	--	.10
TiO_2	.48	--	--	Alkalies	--	--	.42
Fe_2O_3	.92	.82	.41	H_2O	.38	.28	.39
Al_2O_3	.40	--	.43				
CaO	--	.06	.55		99.85	100.25	99.52

1. Botryoidal, from Brazil. Specific gravity 5.533.
2. From Ceylon. Specific gravity 5.72 to 6.025.
3. From Jacupirangi, Brazil. Specific gravity 5.006.

GEOGRAPHICAL OCCURRENCES

Zirconium minerals are widely distributed, but commercial deposits are few.

In the United States, deposits of beach sands have been worked, mostly in conjunction with monazite and titanium (ilmenite), the only one reporting commercial production being that at Mineral City, Jacksonville Beach (formerly Pablo Beach), where Buckman & Pritchard, Inc. (later a subsidiary of the National Lead Co.) operated from 1918 to 1929. More or less extensive deposits of such sands are reported to exist elsewhere along the Atlantic coast; and in the black sands found along the Pacific coast (principally in northwestern California, in Oregon, and in Washington) zircon ranks fifth in order of frequency among the more than 37 minerals identified therein.

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The only other deposit in the United States that has been systematically mined is one of zircon (in pegmatite and pegmatized gneiss) in Henderson County, N. C., near Tuxedo (formerly Zirconia), where mining began on a very small scale as early as 1869; no recorded shipment, however, was made until 1888. Intermittent production continued until 1911, was renewed in 1902, and probably continued until 1916, although accurate figures are not available with respect to output.

Deposits of zircon (in sandstone) at Ashland, Va., and (in pegmatite) at Anderson, S. C., have been mentioned as promising sources of the mineral.

Most of the world's production of zirconium-bearing minerals, however, has come from Brazil, where the only known commercial deposit of baddeleyite (the native oxide) exists, in the States of Sao Paulo and Minas Geraes, in the so-called "Caldas Region." Brazil has important deposits of zircon (the silicate) also, in the States of Bahia, Espirito Santo, and Rio Janeiro, where zircon is associated with the monazite.

Another important source of zirconium is the beach-sand deposit in the Travancore State, India, at the extreme end of the Hindustan Peninsula.

Workable deposits exist also in Madagascar, in the vicinity of Beforona and west of Fianarantsoa, from which regular production has been reported, in relatively small amounts, however.

MINING AND CONCENTRATION

Because of the hardness of the ore, the primitive methods of the emery miners of Naxos were used in the deposits of the Caldas region (States of Minas Geraes and Sao Paulo, Brazil) in 1916, according to Meyer.[29] A fire was built against the exposed face of the ore and kept burning for several hours, and then water was thrown upon the ore to produce fracturing of the mass. According to Cameron,[30] however, dynamite is now being used. In some of the deposits, the ore occurs as lumps and granules in a reddish clay matrix and is mined by open-cut methods. The clay, which readily dries when exposed to the tropical sun, can be separated from the zirconia by a coarse screen.[31] From these deposits the ore is carried about 20 kilometers by carts, loaded on railway cars, and shipped a distance of about 230 miles. The beach deposits, especially those near Victoria (State of Espirito Santo), mined as a by-product of the monazite industry, are surface-mined or quasi surface-mined, there being an overburden of approximately 2 meters of ordinary quartz sand and underlying layers of ilmenite, zircon, and monazite in the proportions of 35 : 25 : 18, respectively. Electromagnetic separators extract first the ilmenite, then the zircon, and finally the monazite.[32]

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29 - Meyer, H. C., Brazilian Zirkite Deposits: Monthly Prices for November, Foote Mineral Co., 1916, pp. 29-31; Schaller, Waldemar T., Zirconium and Rare-Earth Minerals: Reprint from Mineral Foote-Notes, vol. 2, No. 3, Foote Mineral Co. (Inc.), Philadelphia, Pa., Mar., 1918, pp. 6-8.

30 - Cameron, C. R., American consul general, Sao Paulo, Brazil: Trade letter, May 28, 1930, Bur. For. and Dom. Com. file.

31 - Meyer, H. C., Work cited, p. 6.

32 - Cameron, C. R., Work cited.

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In the Florida beach deposits, the sand was loaded into trucks for transportation to the mill or, over part of the beach, was transported over a narrow-gage tramway. An attempt to mine by dredging was not successful, because the rich concentrates do not extend below water level.

In the concentration of zircon or monazite sand, the sand is usually passed over magnetic separators. According to Martens,[33] the Florida beach sands, worked by Buckman and Pritchard (Inc.), were treated first on shaking tables in a wet mill. The table concentrates contained about 20 per cent zircon, together with ilmenite (55 per cent), rutile (6 per cent), monazite (2 per cent), various heavy green silicates (14 per cent), and a little quartz (3 per cent). Dry magnetic treatment removed first the ilmenite and also the so-called "greenspar" (mostly staurolite and epidote), together with most of the monazite, leaving tailings consisting principally of zircon and rutile. These tailings were run over a wet table to eliminate some still remaining quartz and silicate minerals, and the zircon and rutile were separated on an electrostatic machine.

PREPARATION OF THE OXIDE

The oxide is commercially the most important of the various compounds of zirconium. For a complete discussion of the other compounds the reader is referred to the work of Venable,[34] from which the following quotation concerning zirconia (ZrO_2) is taken:

> Preparation of oxide from, or purification of, native zirconia.- For many purposes native zirconia can be used without further treatment. Such uses, for instance, are as a refractory and for furnace linings. However, for the preparation of enamels, salts, and for other uses requiring purity of materials the impurities must be separated. By fusion with an alkali hydrogen sulphate and leaching with water acidulated with sulphuric acid, a solution of the sulphate is obtained. Much of the iron present may be removed by using a small amount of water for the first washing and rejecting this. The solution of the sulphate yields the hydroxide on the addition of ammonia solution. This is dissolved in dilute hydrochloric acid and the zirconyl chloride purified by recrystallization from concentrated hydrochloric acid. On ignition of the chloride zirconia is left, but small amounts of chlorine are persistently retained.
>
> A more economical method has been patented for large-scale production. The ore is heated with excess of lime and an amount of carbon insufficient for the reduction of the lime. Calcium carbide may be used in the place of the carbon. The product is treated with hydrochloric acid, the silica removed, and the zirconyl chloride then purified.

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33 - Martens, H. C., Beach Deposits of Ilmenite, Zircon and Rutile in Florida: Nineteenth Ann. Rept., Florida State Geol. Survey, 1926-27, The State Geological Survey, 1928, pp. 136-140.

34 - Venable, Francis P., Work cited, pp. 36-37.

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Preparation of zirconia from zircons.- The most direct method is by subjecting powdered zircons to the high temperature of the electric furnace. The silica and oxides of iron and certain other metals are volatilized, and the zirconia is left in quite a pure condition.

Another commercial method for the preparation of zirconia in a relatively pure state from the native oxide is suggested by Bradford:[35]

1. Fusion of the finely powdered ore with niter cake (low in iron).

2. Leaching of the mass and separation of the silica by filtering through asbestos mat or other suitable medium.

3. Precipitation of zirconia by commercial sodium thiosulphate after nearly neutralizing the solution with sodic carbonate and precipitating at the boiling point.

4. Filtration of the precipitate, thoroughly washing in a small filter press to remove the solution containing all the iron salts.

5. Ignition of the predried cakes in the fire-clay pots.

By this method, which could be utilized in nitric acid works, an oxide could be produced containing only titania and a little alumina (which would not be harmful for most purposes) and a trace of iron.

Hopkins[36] discusses the extraction (by chemical treatment) of zirconium material from zircon and from baddeleyite, as follows:

From zircon, extraction may be made by several methods: (1) fusion with acid potassium fluoride and extraction with hot water; potassium fluozirconate crystallizes on cooling; (2) fusion with potassium bisulphate and extraction with dilute boiling sulphuric acid; the basic sulphate is left undissolved; (3) heating with NaOH and NaF and extracting with water; the sparingly soluble sodium zirconate is dissolved in HCl, and on evaporation $ZrOCl_2$ separates; (4) fusion with Na_2CO_3 and extracting with water. The zirconate is dissolved in HCl or H_2SO_4.

35 - Bradford, Leopold, Zirconia; Its Possibilities in Metallurgy: Mineral Foote-Notes, vol. 2, No. 7, Foote Mineral Co., July-Aug., 1918, p. 3.
36 - Hopkins, B. Smith, Chemistry of the Rarer Elements: D. C. Heath & Co., New York, 1923, pp. 150-151.

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The preparation of zirconium material from baddeleyite usually consists in the removal of iron, silica, and less commonly titanium. Fe_2O_3 is present in amounts varying from 0.82 per cent to 10.26 per cent, silica 0.19 to 26.30, and titania from a trace to 3.12 per cent. The method of treatment depends upon the purity desired in the product. (1) Boiling with strong HCl or H_2SO_4 removes most of the iron and titanium; ignition with HF and H_2SO_4 removes the silica. (2) For a product free from impurities, it is recommended that the ore be fused with Na_2CO_3 and $Na_2B_4O_7$. The melt is extracted with water and the zirconium salt crystallized out. (3) Fusion with NaOH in an iron crucible, followed by extraction with water and HCl, then precipitation of basic zirconium sulphate yield a pure product. (4) Fusion with $BaCO_3$ at 1400° for two hours gives barium zirconate, which may be dissolved in HCl and the solution evaporated to remove silica. Dissolve the zirconium in acid and allow $ZrOCl_2$ to crystallize. (5) By heating the ore in the electric arc with carbon the nonvolatile zirconium carbide is formed and is easily separated from the volatile silicon carbide. Aqua regia is used to dissolve the ZrC. (6) A method recommended for the large-scale purification of zirkite consists in mixing the ore with sufficient carbon to form silicon carbide, then heating in an arc furnace to a temperature above 2220°. This removes 90-95 per cent of the silicon, but no iron. Next the material is heated in the presence of chlorine or phosgene to remove iron.

As the zirconium compounds prepared directly from the ores invariably contain impurities (especially iron), further purification is necessary. Hopkins[37] presents the following methods:

1. Separation of iron and zirconium.—(1) $Na_2S_2O_3$, added to a boiling hot solution of zirconium salt which contains a little free acid, precipitates zirconia, thoria, and titania, but iron, aluminum, and the rare earths are not precipitated. (2) $(NH_4)_2S$ in the presence of tartaric acid precipitates iron but not zirconium. (3) Ether extracts $FeCl_3$ from a solution containing HCl, but not $ZrCl_4$. (4) Repeated crystallizations of the oxychlorides will separate iron and zirconium. (5) Vaporization of $FeCl_3$ at 200° C. (6) Phenyl hydrazine and sulphurous acid precipitate zirconium but not iron.

2. Separation of titanium and zirconium.—Zirconium may be separated from titanium by (1) boiling with dilute sulphuric and acetic acids, titanium being precipitated; (2) reducing titanium to the trivalent condition and precipitating potassium zirconium sulphate; (3) precipitating basic zirconium phosphate with hydrogen peroxide and sodium phosphate.

37 - Hopkins, B. Smith, Work cited, pp. 151-152.

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3. Separation of zirconia and silica.--Zirconia may be separated quantitatively from silica by fusion with Na_2CO_3; extract the melt with water, filter, evaporate with nitric acid, dehydrate the silica, and expel it with HF and H_2SO_4.

4. Separation of zirconium from titanium and tin.--Titanium and tin may be removed from zirconium by fusion with large excess of $KHSO_4$; dissolve in water and nitric acid, and ignite the SnO_2 residue. Carefully neutralize the solution and precipitate the zirconium with H_2O_2 and from the filtrate precipitate the titanium with NH_4OH.

PREPARATION OF THE METAL

The preparation of pure ductile zirconium is described by De Boer[38] and summarized in Industrial Chemistry and Engineering, as follows:

> There are three ways in which zirconium powder can be produced: (1) By the reduction of zirconium oxide with calcium; (2) by the reduction of zirconium tetrachloride with sodium; and (3) by the reduction of potassium fluozirconate with potassium or sodium.
>
> De Boer claims to have produced very pure coherent zirconium by depositing it on a heated tungsten filament. The zirconium powder prepared by one of the methods listed above is placed in an evacuated flask with a small amount of iodine. At about 500° C. the zirconium and iodine combine to form the tetraiodide, which vaporizes to the filament and is deposited thereon by thermal dissociation.

A method has been worked out by De Boer and Van Arkel for the preparation of pure zirconium and pure hafnium.[39]

Methods for the preparation of amorphous, crystalline, graphitic, and sintered or coherent (solid metal) zirconium are discussed in Bulletin 186 of the Bureau of Mines.[40] The authors thereof agree with Venable (p. 3 of this paper) that it is doubtful whether the crystalline and graphitic forms are pure metal.

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38 - De Boer, J. H., Zirconium: Ind. Eng. Chem., vol. 19, No. 11, Am. Chem. Soc., Nov., 1927, pp. 1256-1259.

39 - Tyler, Paul M., Hafnium: Information Circular, U. S. Bureau of Mines, to be published.

40 - Marden, J. W., and Rich, M. N., Investigations of zirconium with Especial Reference to the Metal and Oxide: Bull. 186, Bureau of Mines, 1921, pp. 35-37.

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WORLD PRODUCTION

The zirconium industry is still in its infancy, and little information is available regarding the annual production of zirconium minerals. The workable deposits of zircon in the United States having ceased to produce, the output is confined to the native oxide, zirkite, mined in Brazil, and the zircon produced in Travancore (India), Brazil, and Madagascar.

Because of the incompleteness of available production figures, no attempt has been made to formulate a comprehensive world table. However, one table is introduced to show the output in the United States and Brazil for the years 1902 to 1919, inclusive, and another to show production in the United States, Brazil, India, and Madagascar for the years 1920 to 1929, inclusive.

Zirconium minerals produced, United States and Brazil, 1902-1919 1/

Year	United States		Brazil	
	Quantity (short tons)	Value	Quantity (short tons)	Value
1902	1	$1,380	12	$3,947
1903	1.5	570	7	1,947
1904	0.5	200	9	3,935
1905	4	1,600	18	5,506
1906	0.5	248	26	5,041
1907	(2)	46	38	8,756
1908	---	------	275	15,151
1909	1	250	117	11,838
1910	---	------	128	23,271
1911	1.6	802	45	16,169
1912	---	------	43	14,772
1913	---	------	1,119	54,767
1914	---	------	237	14,903
1915	---	------	8	2,915
1916	---	------	104	16,647
1917	---	------	532	175,018 Milreis 3/
1918	---	------	2,360	507,019 Do. 3/
1919	---	------	229	$18,478

1/ Figures of production for the United States are taken from Mineral Resources of the United States; those for Brazil are taken from various issues of Commercio Exterior do Brazil, Directoria de Estatistica.

2/ Two hundred and four pounds.

3/ Figures are given in milreis, as the rate of exchange for the year was not available.

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Zirconium minerals produced, United States, Brazil, India, and Madagascar, 1920-1929

Year	United States 1/		Brazil 1/		India (Travancore) 2/		Madagascar 3/
	Quantity (short tons)	Value	Quantity (short tons)	Value	Quantity (short tons)	Value	Quantity (short tons)
1920	-----	-----	597	$25,034	--------	------	3.9
1921	-----	-----	134	6,095	--------	------	13.303
1922	10	4/ $1,000	366	16,844	--------	------	.746
1923	153	4/ 15,300	36	883	162.4	£1,160	27,593
1924	281	4/ 28,100	842	26,137	408.8	2,717	60,21
1925	624	4/ 62,400	137	4,142	645.12	4,608	4.191
1926	1,292	4/129,200	12	563	595.8	2,987	.274
1927	3,646	4/364,600	265	8,313	1,640.8	8,129	-----
1928	(5)	(5)	913	31,048	957.5	4,267	-----
1929	-----	-----	1,187	41,419	--------	------	24.759

1/ Figures for production for the United States are taken from various issues of Mineral Resources of the United States; those for Brazil from issues of Commercio Exterior do Brazil, Directoria de Estatistica.
2/ Figures for India are taken from records of the Geological Survey of India.
3/ Figures for Madagascar, which are the same as the export figures, are taken from Statistique Minière Productions et Exportations, Colonie de Madagascar et Dépendances, Service des Mines. Figures of value are not available.
4/ Estimated by the Bureau of Mines.
5/ Bureau of Mines not at liberty to publish figures.

DOMESTIC PRODUCTION

As early as 1869, zirconium minerals were mined in the United States to the extent of 1,000 pounds; and in 1883 a production of 26 tons was reported. There is no record of further production until 1902, when 1 ton, valued at $380, was mined. Although the mineral was known to exist in commercial quantities in Henderson County, N. C., the demand was too small to encourage any attempts at systematic mining. In 1903, men and children, for a certain price per pound, were washing zircon crystals (practically 100 per cent zircon) out of the soil or kaolinized gangue or breaking them from the harder feldspar in North Carolina. From 1903 to 1911, from ½ ton to 4 tons was produced each year (with the exception of 1908 and 1910), all in Henderson County, N. C. From 1912 to 1919, no minerals were reported in the United States, but in 1922 about 10 tons of zircon was shipped from Florida. Production from Florida increased steadily to 3,646 tons in 1927, and shipments continued into 1928, although the Bureau of Mines was not permitted to publish the figures. In 1929, the plant of Buckman and Pritchard, at Mineral City, Fla., was closed, and subsequently there has been no domestic output of record, although late in 1930 a small production from a new source was contemplated.

IMPORTS

In recent years the zirconium supply of the United States has been mainly imported, principally from Brazil and British India. Until 1918, the exact amount of imports was not known, as the negligible amounts of zirconium

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ores that entered the country, being not separately classified, were included with monazite sand. The table, which follows, indicates imports from July, 1918, to 1929, inclusive.

Zirconium ores (steel-hardening) imported for consumption in the United States, 1918-1929

Year	Pounds	Value
1918--July to December 1/	3,216,659	$77,250
1919	11,023	332
1920	-------	-------
1921	131,016	3,003
1922	67,037	4,072
1923	-------	-------
1924	616,220	4,878
1925	-------	-------
1926	-------	-------
1927	4,488	182
1928	863,685	9,788
1929	2,689,120	35,416

1/ Not separately classified prior to July, 1918.

Imports of zirconium ores and zirconium alloys during 1929, by countries 1/

	Zirconium ore		Ferrozirconium, zirconium, and ferrosilicon	
1929	Pounds	Value	Pounds	Value
Argentina	433,440	$ 5,612	------	-----
Brazil	1,008,000	13,050	------	-----
Canada	------	----	20,221	$ 2,022
France	------	----	22,307	1,290
Germany	------	----	4,520	1,176
India-British	1,247,680	16,754	------	-----
	2,689,120	35,416	47,048	4,488

1/ From records of the Bureau of Foreign and Domestic Commerce, compiled by J. A. Dorsey, of the Bureau of Mines.

MARKETS AND PRICES

The market for zirconium ores is a narrow one, and published quotations covering a period of years are not available for tabulation.

The Foote Mineral Co. (Inc.) issues a price list covering zirkite (crude zirconium oxide), carrying a guaranteed minimum of 65 to 70 per cent of ZrO_2, the following analysis being typical:

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	Per cent
Zirconium dioxide.....	65.66
Silica.....	21.06
Alumina.....	4.95
Titania.....	.92
Iron sesquioxide.....	4.57
Loss on ignition.....	3.01

In 1930, this company quoted $60 a ton for powdered zirkite, either coarse or fine, ground material (95 per cent through 200 mesh) being sold as "Zirkite Cement." On small lots higher prices were charged up to 4½ cents a pound on shipments of 200 to 800 pounds. Lump zirkite is 25 per cent less than powdered zirkite, but higher prices are asked for air-floated material, 99 per cent through 200 mesh. Zirkite fire brick, 75 to 80 per cent zirconium content, is quoted by the same company at $1.10 each for ordinary straights, wedges, or arches.

In 1929, low-grade (60 to 65 per cent) lump ore was obtainable at about $35 to $40 a ton.

Precipitated zirconia white is sold by the Foote Mineral Co., under the trade name "Zirconalba," and by the Titanium Alloy Manufacturing Co. as "Tam Opax." Zirconalba No. 1 (minimum 98 per cent zirconium dioxide), in lots of 100 to 400 pounds, was quoted in 1930 at 75 cents a pound. Zirconalba No. 2 (minimum 80 to 85 per cent zirconium dioxide) was offered at 38 cents a pound, in lots of 500 to 2,000 pounds. Tam Opax (zirconium oxide with no admixtures), according to a price list dated June 20, 1930, in 500-pound barrels, was priced at 30 cents a pound, f.o.b. Suspension Bridge, New York. Of the lower grades of zirconium oxide sold by the Foote Mineral Co., Zirkosil No. 1, minimum 60 per cent zirconium dioxide (ground 80 to 90 per cent through 200 mesh), in 20 to 30 ton lots, was quoted in 1930 at $80 a ton; Zirkosil No. 2, minimum 53 per cent zirconium dioxide (ground 80 to 90 per cent through 200 mesh), in 20 to 30 ton lots, was quoted at $70 a ton.

The above-recorded prices are more or less in line with those of former years. In 1918, imported Brazilian ores were quoted at $100 to $140 a ton, and prepared zirkite varied from 4½ to 7 cents a pound in carload lots. During 1920 and 1921 prices receded to between $50 and $90 for ore, and the price of zirkite bricks (standard shapes) dropped to 45 to 70 cents each. Ore prices have subsequently remained at $50 to $60 (rarely $80) a ton for high-grade lump. Prices of bricks were revised upward, beginning about 1925.

With respect to the oxide, the prices in former years varied so greatly from year to year and from grade to grade that comparisons are difficult. Early in 1920, the pure oxide (99 per cent grade) was quoted at $1.10 to $1.20, increasing by the end of 1921 to $1.25 a pound retail. In 1922, the range of price was from 75 cents to $1.25 for 99 per cent material, but by 1925 the minimum price had become the maximum, as the pure oxide was selling at 56 to 75 cents a pound, which latter price is the 1930 price for the 98 per cent Zirconalba, referred to in a preceding paragraph. Prices during 1926 and 1927 were as low as 35 cents a pound for what was termed "purified oxide."

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During 1929 the price of zirconium metal dropped from $40 to $12 for the 98 to 99 per cent grade and to $8 for the 90 to 95 per cent grade.

High-grade ferrozirconium, powdered or crushed, was quoted by Foote Mineral Co. in 1930 at $1.20, in 200 to 300 pound lots. The following is a typical analysis.

	Per cent
Zirconium.....	71
Titanium.....	4
Aluminum.....	4.5
Carbon.....	4.5
Manganese.....	3.5
Silicon.....	12.5

From July 10, 1930, the Engineering and Mining Journal has been quoting prices on the cheaper alloys as follows: Siliconzirconium (47 to 52 per cent silicon and 35 to 40 per cent zirconium) at 18 to 21 cents a pound; zirconium-ferrosilicon (12 to 15 per cent zirconium and 39 to 43 per cent silicon) at $103.50 to $108.50 a gross ton.

LIST OF IMPORTERS, PRODUCERS, AND DEALERS

United States

Abel Brothers & Co., 16 Maiden Lane, New York, N. Y.
M. C. Cadwallader, 1317 La Veta Terrace, Los Angeles, Calif.
Charlotte Chemical Laboratories, Charlotte, N. C.
(Successors to Oliver Quartz Co.)
Crucible Steel Co. of America, 17 East 42d St., New York, N. Y.
Foote Mineral Co., 1609 Summer St., Philadelphia, Pa.
General Minerals Corporation, Suite 317-319, Mather Bldg., Washington, D.C.
Gordon & Rogers, 141 Broadway, New York, N. Y.
The Harshaw Chemical Co. of New York, 150 Nassau St., New York, N. Y.
(Successors to The Superfos Co., Inc.)
L. Heller & Son (Inc.), 15 West 47th St., New York, N. Y.
O. Hemmel Co., 211 Fourth Ave., Pittsburgh, Pa.
Philip S. Hoyt, Las Tablas, N. Mex.
E. J. Lavino & Co., Bullitt Bldg., Philadelphia, Pa.
Levere Co., 94 Canal St., New York, N. Y.
Metal & Thermit Corporation, 120 Broadway, New York, N. Y.
Pennsylvania Salt Co., Juniper and Chestnut Sts., Philadelphia, Pa.
Philipp Bros. (Inc.), Woolworth Bldg., New York, N. Y.
August Rassweiter, 159 North State St., Chicago, Ill.
E. Schaaf Regelman, 220 Broadway, New York, N. Y.
Rogers, Brown & Crocker Bros. (Inc.), 21 East 40th St., New York, N. Y.
S. R. Scott & Co., 39 Broadway, New York, N. Y.
Suffern & Co., 135 Broadway, New York, N. Y.
M. L. Thomas, Crown Point Chemical Co. (Inc.), Crown Point, N. Y.
Union Carbide & Carbon Corporation, 30 East 42d St., New York, N. Y.
Varlacoid Chemical Co., 15 Moore St., New York, N. Y.
Welsbach Co., Gloucester, N. J.

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Foreign Countries

A. J. Byington, Rua Alvares Penteado 4, Sao Paulo, Brazil
(owner of deposits).
Algernon Lewin Curtis, P. O. 61, Westmoor Laboratory, Chatteris, England.
A. C. de Freitas & Co., Hamburg, Germany.[41]
Elias Goebel & Son, Epterode, in Hessen Nassau, Germany
(manufacturers of crucibles of all kinds).
John Gordon, Rua Visc. Itaborahy 75, Rio de Janeiro, Brazil
(owner of monazite-sand deposits, which contain zircon).
W. C. Heraeus, Hanau, Germany.
Hopkin & Williams (Ltd.), 16 Cross St., Hatton Garden, London, England.
Mauricio Isralson, R. General Camara, 106 Sob., Rio de Janeiro, Brazil.
David McKnight, Rua Alamoda Barros 38, Sao Paulo, Brazil
(owner of deposits).
P. S. Nicholson & Co., Caixa 91, Rio de Janeiro, Brazil.
S. A. Casa Nicholson, Rua Theophilo Ottoni 45, Rio de Janeiro, Brazil
(owner of monazite-sand deposits, which contain zircon).
Luiz de Rezende & Co., Rua Ouidor, Rio de Janeiro, Brazil.
Charles Spitz, Rio de Janeiro, Brazil.[42]
Thorium (Ltd.), Ilford, Essex County, England
(associated with Hopkin and Williams).
Wesenfeld, Dicke & Co., Barmen, Germany.

LIST OF POSSIBLE BUYERS

United States

Abel Bros. & Co. (Inc.), 16 Maiden Land, New York, N. Y.
Jerome Alexander, 50 East 41st St., New York, N. Y.
Eimer & Amend, 201-209 East 13th St., New York, N. Y.
The Exolon Co., Commercial Ave. and Erie R. R., Blasdell, N. Y.
Foote Mineral Co., 1609 Summer St., Philadelphia, Pa.
The Harshaw Chemical Co. of New York, 150 Nassau St., New York, N. Y.
(Successors to the Superfos Co., Inc.)
O. Hommel Co., 209-211 Fourth Ave., Pittsburgh, Pa. (Buyer of ore)
Juergens & Anderson Co., 53 East Washington St., Chicago, Ill.
Levere Co., 94 Canal St., New York, N. Y.
A. D. Mackay, 26 Cortlandt St., New York, N. Y.
F. E. Morse Co., 218 South Wabash Ave., Chicago, Ill.
National Sales Corporation, 31-35 East 13th St., Cincinnati, Ohio.
Norton Co., Worcester, Mass.
Philipp Bros. (Inc.), Woolworth Bldg., New York, N. Y.

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41 - This company had a contract concerning monazite sand with the Brazilian Government. The De Freitas properties are now being worked by the French Societe Miniere.

42 - Agent for the Société Minière, a French company in which Rezende & Co. is said to be interested.

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The Roessler & Hasslacher Chemical Co., 10 East 40th St., New York, N. Y.
Rogers Brown & Crocker Bros. (Inc.), 21 East 40th St., New York, N. Y.
Wm. H. Taggart, 17 South Desplaines St., Chicago, Ill. (Buyer of silicate.)
Titanium Alloy Manufacturing Co., 94 Fulton St., New York, N. Y.; 6007 Euclid Ave., Cleveland, Ohio.
Varlacoid Chemical Co., 15 Moore St., New York, N. Y.
Vitro Co., 928 Fulton Bldg., Pittsburgh, Pa.

Foreign Countries

Algernon Lewin Curtis, P. O. 61, Westmoor Laboratory, Chatteris, England.
Deutsche Gasglühlicht Gesellschaft (Auergesellschaft), Berlin, Germany.
Etablissements G. Devineau, 26 Rue Lafayette, Paris, France.
Messrs. Augusto de Freitas (Ltd.), Hamburg, Germany.
David Gething, Landore Copper Works, Landore, S. O. Glamorgan, S. E. Wales.
L. le Personne & Co., 99 Cannon St., London, E. C. 4, England.
James H. Mason Smelting Co., 803 St. Clarens Ave., Totonto-2, Canada.

PATENTS RECENTLY REPORTED (1929 AND 1930)

BECKET, FREDERICK M. (To Electro Metallurgical Co.). Zirconium-treated Iron-Chromium Alloy. U. S. Patent 1,689,276, Oct. 30, 1928; Chem. Abs., vol. 23, No. 1, Jan. 10, 1929, p. 98.

Wrought articles such as tubing are formed of a ferrous alloy containing 0.008 per cent of zirconium, or a little more, and 10 to 60 per cent of cerium. The alloy has working properties superior to those of an alloy free from zirconium but otherwise of similar composition.

BECKET, FREDERICK M. Zirconium-treated Alloy. U. S. Patent 1,689,630; Foote-Prints, vol. 2, No. 1, 1929, p. 34.

A ferrous alloy containing 10 to 20 per cent of chromium and 0.003 per cent or more of zirconium is used for wrought articles such as tubing. The zirconium distinctly improves the working properties of the alloy.

DEUTSCHE GASGLÜHLICHT AUER-GES. Treating Ores of Titanium, Zirconium, etc. British Patent 291,004, May 23, 1927; Chem. Abs., vol. 23, No. 5, Mar. 10, 1929, p. 1099.

Ores of titanium and zirconium and other rare earths are sulphatized with H_2SO_4, and the resulting sulphates are roasted to form oxides. SO_2 and SO_3 evolved are passed over finely divided ores in the presence of O or air to form additional sulphates, and the partially sulphatized ore is then treated with H_2SO_4. The process may be carried out in two rotary furnaces.

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DEUTSCHE GASGLUHLICHT AUER-GES. M. B. H. Preparation of Pure Zirconium Sulphate from Zirconium Ores Decomposed by Sulphuric Acid. German Patent 434,987, Sept. 26, 1923; Chem. and Ind., vol. 49, No. 27, London, July 4, 1930, p. 612.

The concentrated, slightly acid solution of zirconium sulphate obtained by digesting the ore with sulphuric acid is treated with sulphuric or hydrochloric acid to precipitate zirconium sulphate. This is redissolved in dilute acid, the solution neutralized and boiled to precipitate a basic sulphate, and this salt is redissolved and reprecipitated by either of the above-mentioned methods to eliminate the last traces of iron and titanium.

DEUTSCHE GOLD-UND-SILBER-SCHEIDEANSTALT (To Roessler, 7, Weissfrauenstrasse, Frankfort-on-Main, Germany, and L. Weiss, 20, Mittelweg, Frankfort-on-Main, Germany). Tin, Titanium and Zirconium Oxides. British Patent 327,142, Dec. 27, 1928; Chem. Age, vol. 22, No. 570, London, May 31, 1930, p. 519.

Pigments and turbidity agents for vitreous enamels are obtained by treating soluble compounds of tin, titanium, and zirconium, with or without limited quantities of solvents, with substances capable of converting them into oxides, such as alkaline lyes, steam, or ammonia. The oxides or hydroxides obtained are converted into a voluminous form by heating to 500-800° C. in the case of pigments, or 900-1500° in the case of turbidity agents. The reaction may take place in the vapor stage, in which case the subsequent heating may be omitted. Reference has been directed by the comptroller to Specification No. 28,565/1908, 203,352, 206,284, and 296,730.

KARL, A. Zirconium Oxide. British Patent 314,526, Aug. 21, 1929; Jour. Am. Ceram. Soc., vol. 12, No. 11, Nov., 1929, p. 848.

Zirconium oxide is obtained from an alkali zirconate by bringing the latter into solution as sulphate and then precipitating the hydroxide, as by hydrolysis in neutral solution. Simultaneous precipitation of associated impurities such as iron, titanium, or aluminum is prevented by first reducing the solution with a powerful reducing agent such as nascent hydrogen, sulphurous acid, or sodium hyposulphite. It is stated that the process is applicable also to the production of metal oxides similar to zirconium oxide.

KIERNAN, WM. PHILIP. Preparation of Zirconium. U. S. Patent 1,760,413, May 27, 1930; Jour. Am. Ceram. Soc., Abs. Bull., vol. 9, No. 8, Aug., 1930, p. 652.

The process of producing formed articles of zirconium, which comprises producing a relatively pure coarse-metal powder of the metal, compacting the powder, heating the compacted article to a low temperature in a high vacuo to substantially degasify the compacted metal powder, sintering the degasified article at a high temperature approximately, but below the fusion point thereof in the same high vacuo, and thereafter subjecting the sintered article to mechanical deformation at temperature approximating 800° C.

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